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# HYDROGEN STORAGE ALLOY MATERIAL AND PROCESS FOR PRODUCING THE SAME

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## TECHNICAL FIELD

The present invention relates to a hydrogen storage alloy material containing dispersed nanoparticles of a hydrogen storage metal, and a production method therefor, wherein a Zr-Pd amorphous alloy doped with at least one metal selected from the group of Pt, Au, Fe, Co and Ni is used as a precursor. In particular, the hydrogen storage alloy material of the present invention is usable as a hydrogen storage container excellent in hydrogen absorption (storage)/desorption characteristics.

## BACKGROUND ART

Heretofore, there have been known various hydrogen storage alloys, such as an Mm (Misch metal)-Ni-based alloy and a Ti-V-based alloy. In particular, the Mm-Ni-based and Ti-V-based alloys are used as an electrode material for batteries and a hydrogen storage material. These conventional hydrogen storage alloys have problems about insufficient capacity when used as an electrode material for batteries, and excessively large size in products when used as a hydrogen storage material, due to its low hydrogen storage amount.

As measures for increasing the hydrogen storage amount, various efforts have been made for the development of hydrogen storage alloy processing and the control of microstructure in alloys, such as nano-crystallization/amorphization of an alloy structure based on a mechanical alloying process or a rapid liquid quenching process, as well as researches on new alloys.

For example, an amorphous Mg-Ni-based hydrogen storage alloy capable of absorbing (storing) and desorbing hydrogen even in room temperatures has been developed that is prepared by amorphizing an ordinary conventional Mg-Ni-based alloy through a mechanical alloying process (see, for example, Patent Publications 1 and 2). There has also been known a hydrogen storage metal body consisting only of Pd metal fine particles (see Patent Publication 3). On the other hand, it is pointed out that a further breakthrough is required to make the amorphous

alloy-based hydrogen storage alloy fit for practical use, because most of the amorphous alloy-based hydrogen storage alloys has no plateau.

Moreover, a production method based on a mechanical alloying process or a mechanical grinding process can provide final products only after long hours of powder mixing and alloy processing, which leads to a problem about poor productivity.

[Patent Publication 1] Japanese Patent Laid-Open Publication No. 11-061313

[Patent Publication 2] Japanese Patent Laid-Open Publication No. 11-269572

[Patent Publication 3] Japanese Patent Laid-Open Publication No. 04-311542

## DISCLOSURE OF THE INVENTION

For the purpose of improving hydrogen storage characteristics, it has been attempted to subject a hydrogen storage metal or alloy to a mechanical alloying process or a mechanical grinding process so as to obtain a fine-grained polycrystalline structure. In view of the above circumstances, the inventors carried on various researches for obtaining a hydrogen storage alloy material having a microstructure with dispersed nanoparticles of a hydrogen storage metal, and ability of more efficiently absorbing and storing hydrogen.

As the result of the researches, through a process of preparing an alloy of Zr and a hydrogen storage metal of Pd, expressed by the following formula:  $Zr_{100-x}Pd_x$  (x is a given atomic %, such as = 35, 50 or 60), oxidizing the alloy to selectively oxidize Zr in the alloy, the inventors obtained a material having a microstructure where ultrafine nanoparticles of the hydrogen storage metal Pd aggregated/formed from an amorphous state are dispersed in a parent phase of  $ZrO_2$  (zirconia).

The inventors also found that this material has a hydrogen storage amount of 2.5 weight % or more in a weight ratio relative to Pd contained in the material, which is far greater than a hydrogen storage amount (reported value) in a material consisting only of Pd in the same weight as that of Pd contained in the material ("Journal of the Japan Institute of Metals", page 515, the Japan Institute of Metals, 10/01/2000).

Further, the inventors have achieved improvement in hydrogen desorption capacity of this hydrogen storage alloy.

Specifically, according to a first aspect of the present invention, there is provided a hydrogen storage alloy material prepared by subjecting an amorphous alloy having a composition, in atomic %, expressed by the following formula:  $Zr_{100-a-b}Pd_aM_b$  (wherein  $15 \leq a \leq 40$ ,  $0 < b \leq 10$ , and M is at least one metal selected from the group consisting of Pt, Au, Fe, Co and Ni), to a heat treatment in air or an oxygen atmosphere. The hydrogen storage alloy material has a structure where the Pd, the metal M and one or more compounds thereof are dispersed in a parent phase of  $ZrO_2$  in the form of ultrafine particles.

The hydrogen storage alloy material of the present invention may exhibit a hydrogen storage amount of 2.5 weight % or more in a weight ratio relative to Pd contained in the material.

According to a second aspect of the present invention, there is provided a hydrogen storage/transportation container comprising a hydrogen storage/transportation medium consisting of the hydrogen storage alloy material set forth in the first aspect of the present invention.

According to a third aspect of the present invention, there is provided a method for producing the hydrogen storage alloy material set forth in the first aspect of the present invention, which comprises: preparing a melt of a master alloy formed through a melting process; rapidly solidifying the melt at a cooling rate of  $10^4$  K/s or more to form the amorphous alloy; and subjecting the amorphous alloy to an oxidizing heat treatment in air or an oxygen atmosphere at 250 to 350°C to selectively oxidize the alloy element Zr so as to allow the Pd, the metal M and one or more compounds thereof to be dispersed in a parent phase of  $ZrO_2$  in the form of nanoparticle-size ultrafine particles.

In the hydrogen storage alloy material set forth in the first aspect of the present invention, Pd (atomic %; "a") is contained in the range of 15 to 40 atomic %. If a content of Pd is less than 15 atomic % or greater than 40 atomic %, hydrogen absorption/desorption capacities will be lowered, resulting in loss of practicality. A hydrogen desorption capacity can be improved by adding 10 atomic % or more of the metal M to Pd having a high hydrogen absorption capacity. Preferably, the metal M is added in the range of 2 to 7 atomic %. If a total content of Pd and the metal M (atomic %; "a + b") is less than 15 atomic % or greater than 50 atomic %, a content of Zr will be in the range of 85 to 50 atomic %, and thereby an alloy prepared by a rapid solidification process cannot have an amorphous structure. Moreover, the content of Pd

deviating from the optimum range causes a change in microstructure. These lead to lowered hydrogen absorption/desorption amounts, resulting in loss of practicality. Preferably, a content of Zr is 65 atomic % or more in view of facilitating the formation of an amorphous structure.

In the hydrogen storage alloy material of the present invention where ultrafine particles  
5 consisting of Pd, the metal M and one or more compounds thereof and having a nanoparticle size of about 20 nm or less are dispersed in  $ZrO_2$ , Pd contributes mainly to hydrogen absorption/storage. A hydrogen storage amount in a weight ratio relative to Pd contained in the material is 2.5 weight % or more, preferably 3 weight % or more. In the material of the present invention, the parent phase of  $ZrO_2$  essentially has no hydrogen storage characteristic. Thus, a  
10 hydrogen storage amount was evaluated based on only a weight of Pd contained in the material, which is derived by subtracting a weight of the  $ZrO_2$  from the total weight of the material. This value is the above hydrogen storage amount in a weight ratio relative to Pd contained in the material (Pd weight-based hydrogen storage amount).

In the present invention, the alloy prepared by a rapid solidification process is used as a  
15 starting material. This makes it possible to form an amorphous structure in the material without segregation. This starting material is oxidized to preferentially or selectively oxidize Zr which is one element of the Zr-Pd alloy, so that the element Pd in an amorphous state is aggregated to form ultrafine particles consisting of the Pd, the metal M and one or more compounds thereof and having a nanoparticle size of about 20 nm or less and clean hetero-phase boundaries without  
20 segregation, and the ultrafine particles are dispersed in the parent phase of  $ZnO_2$ . Thus, it is not desirable that the starting material exhibits crystallinity.

In the present invention, while a process for preparing the amorphous Zr-Pd-based alloy as a starting material is not limited to a specific one, it is preferable to prepare the starting material by rapidly solidifying a molten master alloy at a cooling rate of  $10^4$  K/s or more through a liquid  
25 quenching process, such as a single-roll process, a twin-roll process, a gas atomization process or a melt extraction process.

The method for producing the hydrogen storage alloy material having dispersed nanoparticle-size ultrafine hydrogen-storage-metal particles according to the first aspect of the present invention will be described below.

Firstly, a master alloy is formed through a melting process in such a manner as to have an intended alloy composition. It is preferable to perform the melting process in an arc melting furnace filled with an inert atmosphere, such as argon. Then, the master alloy is re-molten, and the obtained melt is rapidly solidified at a cooling rate of  $10^4$  K/s or more to form a rapidly-solidified alloy.

This rapid solidification process at a cooling rate of  $10^4$  K/s or more may be achieved by using one of various conventional processes, such as a single-roll process, a twin-roll process, a gas atomization process or a rotary submerged spraying process. In the present invention, it is preferable to use the single-roll process having an advantage of being able to relatively easily control a cooling rate. A cooling rate of less than  $10^4$  K/s causes difficulty in forming an amorphous structure.

Then, the obtained starting material consisting of the amorphous alloy in the form of a foil, powder or wire is oxidized in air or an oxygen atmosphere at about 250 or 350°C for about 24 hours. The heating process is not limited to a specific one, but any suitable heating process excellent in productivity may be used. In view of allowing only Zr in the material to be selectively oxidized while suppressing excessive oxidization of Pd and other elements, it is undesirable to heat the material up to a high temperature of 400°C or more. If the heating temperature is less than 250°C, a sufficient oxidization cannot be obtained.

The state of metal particles precipitated in the parent phase of  $ZrO_2$  is varied depending on a content of Pd and a kind and content of the metal M. For example, when a content of the metal M is reduced, (1) Pd-M particles and surplus-Pd particles or (2) an oxide thereof will be precipitated in the  $ZrO_2$ , or (3) Pd and M will be separately precipitated in the  $ZrO_2$ . When a content of the metal M is increased, (1) Pd-M alloy particles (compound: intermetallic) and surplus-M particles or (2) an oxide thereof will be precipitated in  $ZrO_2$ , or (3) Pd and M will be separately precipitated in  $ZrO_2$  (if Pd and M are hardly incorporated into each other as a solid solution).

## BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will now be specifically described in connection with Inventive and

## Comparative Examples.

### [Example 1 & Comparative Examples 1 and 2]

Each of master alloys having various compositions as shown in Table 1 was formed through a melting process using an arc melting furnace in an argon atmosphere. Then, the master alloy was subjected to a single-roll process to form a flat-shaped rapidly-solidified thin strip. More specifically, in the single-roll process, the master alloy was molten using a quartz nozzle under an argon atmosphere, and the molten master alloy was injected at  $0.3 \text{ kg/cm}^2$  onto a copper roll having a diameter of 20 cm and rotating at 4000 rpm, through a quartz nozzle having a nozzle-hole diameter of 0.3 mm, so that the molten master alloy was rapidly solidified and formed as an amorphous alloy foil having a width 1 mm and a thickness of 20  $\mu\text{m}$ . Then, this amorphous alloy foil was oxidized in air or an oxygen atmosphere at 280 to 350°C for about 24 hours. The obtained alloy was crushed or powdered into a size of about 30  $\mu\text{m}$ , and subjected to a measurement of hydrogen storage amount under temperatures of 50°C and 150°C.

The measurement was performed using a Sieverts-type PCT-characteristics measuring apparatus (made by Suzuki Shokan Co., Ltd., Japan) under the condition of hydrogen pressurization of up to 5 MPa. Further, before an operation for hydrogen absorption, a phase identification using an X-ray diffraction process was performed to determine whether a crystal phase was precipitated.

In Table 1, Pd weight-based hydrogen storage amount in Inventive Examples 1 and 2 means a hydrogen storage amount in a weight ratio relative to Pd + Ni contained in the material, and Pd weight-based hydrogen storage amount in Comparative Example 5 means a hydrogen storage amount in a weight ratio relative to Au contained in the material.

Table 1

	Composition of starting material (at. %)	Measurement temperature of hydrogen storage characteristics (°C)	Hydrogen storage amount of entire material (wt. %)	Pd weight-based hydrogen storage amount (wt. %)	Pd weight-based hydrogen desorption amount (wt. %)	Structure	Phase of starting material
Inventive Example 1	Zr <sub>65</sub> Pd <sub>30</sub> Ni <sub>5</sub>	150	0.71	2.30	1.21	Pd nanoparticles +ZrO <sub>2</sub>	amorphous
Inventive Example 2	Zr <sub>65</sub> Pd <sub>30</sub> Ni <sub>5</sub>	50	0.78	2.51	1.57	Pd-Ni alloy nanoparticles +ZrO <sub>2</sub>	amorphous
Comparative Example 1	Zr <sub>65</sub> Pd <sub>35</sub>	150	0.71	2.19	0.54	Pd nanoparticles +ZrO <sub>2</sub>	amorphous
Comparative Example 2	Zr <sub>65</sub> Pd <sub>35</sub>	50	0.84	2.58	1.33	Pd nanoparticles +ZrO <sub>2</sub>	amorphous
Comparative Example 3	Zr <sub>50</sub> Pd <sub>50</sub>	150	0.45	0.95	0.32	Pd coarse particles +ZrO <sub>2</sub>	crystalline
Comparative Example 4	Zr <sub>50</sub> Pd <sub>50</sub>	50	0.59	1.26	0.61	Pd coarse particles +ZrO <sub>2</sub>	crystalline
Comparative Example 5	Zr <sub>70</sub> Pd <sub>30</sub>	150	0.44	0.09	0.09	Au nanoparticles +ZrO <sub>2</sub>	amorphous
Comparative Example 6	Pd (reported value)	150	0.65	0.65	0.65	Pd (polycrystalline structure of coarse particles)	crystalline
Comparative Example 7	Pd (reported value)	50	0.69	0.69	0.69	Pd (polycrystalline structure of coarse particles)	crystalline

As is clear from Table 1, in Inventive Examples 1 and 2 using a Zr-Pd-Ni amorphous alloy as a starting material, a hydrogen storage amount of the entire material is 0.7 weight % or more. In contrast, Comparative Examples 3 to 5 having a composition deviating from the composition range of the present invention (each of Comparative Examples 3 and 4 contains Pd in an amount beyond the range allowing the starting material to be formed as an amorphous structure, and Comparative Example 5 contains Au having no hydrogen storage capacity in place of Pd) exhibits a hydrogen storage amount inferior to those of Inventive Examples 1 and 2.

As mentioned above, the parent phase of ZrO<sub>2</sub> in the hydrogen storage alloy material of the present invention essentially has no hydrogen storage characteristic, and thereby a value evaluated based on only a weight of Pd contained in the material, which is derived by subtracting a weight of the ZrO<sub>2</sub> from the total weight of the material, is a hydrogen storage amount in a

weight ratio relative to Pd contained in the material (Pd weight-based hydrogen storage amount). Referring to Table 1 for this value, while the Pd weight-based hydrogen storage amount is 2 weight % or more in each of Inventive Examples 1 and 2 and Comparative Examples 1 and 2, it is less than 1.5 weight % in each of Comparative Examples 3 to 5. Comparing with a hydrogen storage amount (reported value) in each of Comparative Examples 6 and 7 consisting only of Pd, each of Inventive Examples 1 and 2 has an absorption efficiency 3 to 4 times greater than those of them. This shows that the microstructure with dispersed hydrogen-storage-metal nanoparticles produced by the method of the present invention drastically enhances an original hydrogen storage capacity of the hydrogen storage metal.

In addition, each of Inventive Examples 1 and 2 using the starting material prepared by substituting Ni as the metal M for 5 atomic % of Pd in the total Pd content of Comparative Example 1 or 2 has approximately the same hydrogen storage amount as those of Comparative Example 1 and 2. However, when a difference between a maximum hydrogen storage amount under a maximum equilibrium hydrogen pressure of about 4.5 MPa in the aforementioned measuring apparatus, and a residual hydrogen storage amount after hydrogen desorption is calculated as a hydrogen desorption amount in a weight ratio relative to Pd contained in the material (Pd weight-based hydrogen desorption amount), the Pd weight-based hydrogen desorption amount in each of Inventive Examples 1 and 2 is superior to those of Comparative Example 1 and 2. This verifies that a hydrogen storage alloy having higher practicality can be produced by adding the metal M.

## INDUSTRIAL APPLICABILITY

The hydrogen storage alloy of the present invention using as a precursor the Zr-Pd-M (M is at least one metal selected from the group of Pt, Au, Fe, Co and Ni) amorphous alloy has excellent hydrogen absorption (storage)/desorption efficiency. Thus, this hydrogen storage alloy can be suitably used as a hydrogen storage material in various fields, particularly a stationary hydrogen storage facility, and can serve as a guideline for a structural design of a material capable of efficiently incorporating hydrogen therein. Further, the production method of the present invention makes it possible to prepare the precursor comprising the Zr-Pd-M (M is



at least one metal selected from the group of Pt, Au, Fe, Co and Ni) amorphous alloy using a single-roll process allowing a serial production and oxidize the precursor so as to provide highly-efficient hydrogen storage ally, in a simple and easy manner.